# Radiation-induced grafting of styrene onto poly(tetrafluoroethylene) (PTFE) films. I. Effect of grafting conditions and properties of the grafted films

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**Abstract: Radiation-induced grafting of styrene onto poly(tetrafluoroethylene) (PTFE) films was studied by a simultaneous irradiation technique. Grafting was carried out using $\gamma$-radiation from a $^{60}$Co source at dose rates of 1.32–15.0 kGy h$^{-1}$ at room temperature. The effects of type of diluent, dose rate, irradiation dose, and the initial monomer concentration in the grafting solution on the degree of grafting were investigated. The degree of grafting was found to be strongly dependent upon the grafting conditions. The dependence of the initial rate of grafting on the dose rate and the initial monomer concentration in the grafting solution was found to be in the order of 0.6 and 1.7, respectively. The chemical structure and the crystallinity of the grafted PTFE films were studied by means of Fourier-transform infrared, (FTIR), electron spectroscopy for chemical analysis (ESCA) and X-ray diffractometry (XRD).**



**Keywords:** radiation-induced grafting; styrene; PTFE film; grafted film

## INTRODUCTION

Radiation-induced grafting of hydrophilic monomers onto fluorinated polymers has frequently been used to prepare ion-exchange membranes for various applications.[1–6] This technique has been found to be convenient because the commercially available polymeric films can be modified without any need to transform them into thin foil.[7] Moreover, the percentage of grafting can be controlled by proper selection of grafting conditions.[8] Fluorinated polymers are favoured for their outstanding chemical as well as thermal stability and mechanical strength.[9] Monomers such as acrylic acid,[10] vinyl acetate,[11] *N*-vinyl-2-pyrrolidone,[12] 4-vinyl pyridine,[13] methyl methacrylate,[14] acrylamide[15] and styrene[16–18] have been grafted onto PTFE films on various occasions using simultaneous and pre-irradiation techniques. Many studies have been published on grafting of a weak acid functionality such as acrylic acid onto PTFE films,[19–24] but only a few on the grafting of a strong acid functionality such as sulphonic acid.[25,26]

Ion-exchange membranes bearing sulphonic acid groups are commonly prepared by grafting of styrene onto fluorinated polymers, and the graft copolymer is subsequently sulphonated.[27] The use of such an indirect method, rather than direct grafting of vinyl monomer having sulphonic acid groups as in case of acrylic acid, is because of the incompatibility between the highly ionized sulphonic acid groups with its hydration sphere and the polymer backbone. This effect hinders monomer diffusion into the bulk of the polymer backbone and suppresses the polymerization reaction, as happened when vinyl sulphonic acid was grafted onto polyethylene.[28]

A number of studies have reported the grafting of styrene onto other fluorinated polymers such as poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)[29,30] and partially fluorinated polymers such as poly(ethylene-*co*-tetrafluoroethylene) (ETFE)[31] poly-(vinylidene fluoride) (PVDF)[32] to produce graft copolymer to host sulphonic acid groups.

In our previous studies, grafting of styrene onto poly(tetrafluoroethylene-co-perfluorovinyl ether) PFA and FEP films was investigated using a simultaneous irradiation technique.[33,34] The degree of grafting was found to be strongly dependent upon the grafting

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conditions. The present study aims to extend our work by grafting of styrene onto PTFE films to produce another copolymer to host sulphonic acid functionality. Kinetics of the grafting were investigated to determine the effects of grafting conditions such as type of solvent, irradiation dose, dose rate and the initial monomer concentration on the grafting. The chemical structure and crystallinity of the grafted films were investigated to confirm the grafting of styrene and to monitor the structural changes induced by grafting before sulphonation.

## EXPERIMENTAL

### Materials

PTFE film of 90 μm thickness (Porghof, USA) was used as a base polymer. Styrene of purity more than 99 % (Fluka) was used as a grafting monomer without any further purification. Other chemicals were reagent grade and were used as received.

### Grafting procedure

Square pieces (5 cm × 5 cm) of PTFE film were washed with acetone and then dried in a vacuum oven (10 mbar) at 60 °C to constant weight. The dried films were placed with a styrene solution of known concentration into glass ampoules and the grafting mixture was deaerated by bubbling with nitrogen for 8–10 min and the ampoule was sealed. The ampoule was irradiated at ambient temperature using $\gamma$-rays from a $^{60}$Co source (Jlshepher and Associates, Model 109, USA) at dose rates in the range 1.32–15.00 kGy h$^{-1}$ for the required period of time. The grafted films were removed, washed with toluene and soaked therein overnight to remove the residual monomer and homopolymer adhering to the films' surfaces. The grafted films were washed free of toluene with methanol, then dried in vacuum oven at 80 °C to constant weight. The degree of grafting ($G$%) was calculated using the equation

$$G(\%) = \frac{W_g - W_o}{W_o} \times 100 \qquad (1)$$

where $W_g$ and $W_o$ are the weights of grafted and original PTFE films, respectively.

### Swelling measurements

Swelling measurements were carried out by immersing 90 μm PTFE film in styrene having various concentrations for 4 days and at room temperature. The film was removed and the excess solution on the surface wiped by blotting paper. The film was then weighed and the degree of swelling determined gravimetrically.

### Characterization of the grafted films

The chemical structures of original and grafted PTFE films were determined using a Mattson 6020-Galaxy FTIR spectrophotometer equipped with an ATR accessory having a KRS5 crystal with a face angle of 45 ° and by a Kratos XSAM-HS electron spectrometer (electron spectroscopy for chemical analysis, ESCA) operating in FAT mode with overall resolution of 1.3 eV. A low X-ray flux of the non-monochromatized MgK$\alpha$ line, normally operated at 10 mA and 12 kV, was used to minimize the charging effect. The chamber pressure was set at a value of not less $8 \times 10^{-9}$ torr. Binding energies were calibrated using a gold standard (Au4$f_{7/2}$ at 84 eV). Samples were mounted on the sample holder with double-sided adhesive tape.

The crystallinity changes induced by styrene grafting were determined using a Philips PW 1830 X-ray diffractometer. The diffractograms were recorded at ambient temperature and with $2\theta$ in the range 5–60 ° by means of CuK$\alpha$ radiation ($\lambda = 1.54$ Å) monochromated with a nickel filter.

## RESULTS AND DISCUSSION

### Effect of grafting conditions

*Type of solvent*

The effect of the type of solvent on the degree of grafting of styrene having an initial concentration in the starting solution of 5.77 mol l$^{-1}$ onto PTFE films at various irradiation times is shown in Table 1. The solvents employed include methanol, benzene and dichloromethane. No inhibitor was added. It is found that dilution of styrene with dichloromethane causes a dramatic increase in the degree of grafting compared to that obtained upon dilution with methanol and benzene, and no homopolymer was observed. These results can be explained by considering the nature of the three solvents and the solubility of polystyrene homopolymer in the various grafting mixtures. The higher grafting levels obtained upon the dilution of styrene with dichloromethane is attributed to the slowdown in the termination of the growing polystyrene chains under the influence of the low chain transfer constant (0.15)[35] and the electron acceptor nature of dichloromethane. This is accompanied by complete solubility of polystyrene homopolymer that might be formed in the grafting mixture. Therefore,

**Table 1.** Effect of the type of solvent on the degree of grafting of styrene[a] onto PTFE films at various irradiation times

| | *Degree of grafting* (%) | | | |
|---|---|---|---|---|
| *Solvent* | 3.8 h | 15.2 h | 22.7 h | *Remarks* |
| Methanol | 3.6 | 7.4 | 5.1 | Much homopolymer formed |
| Benzene | 4.5 | 19.0 | 21.6 | Little homopolymer formed |
| Dichloromethane | 8.5 | 42.8 | 63.2 | No homopolymer formed |

[a] Initial concentration in the starting solution 5.77 mol l$^{-1}$.

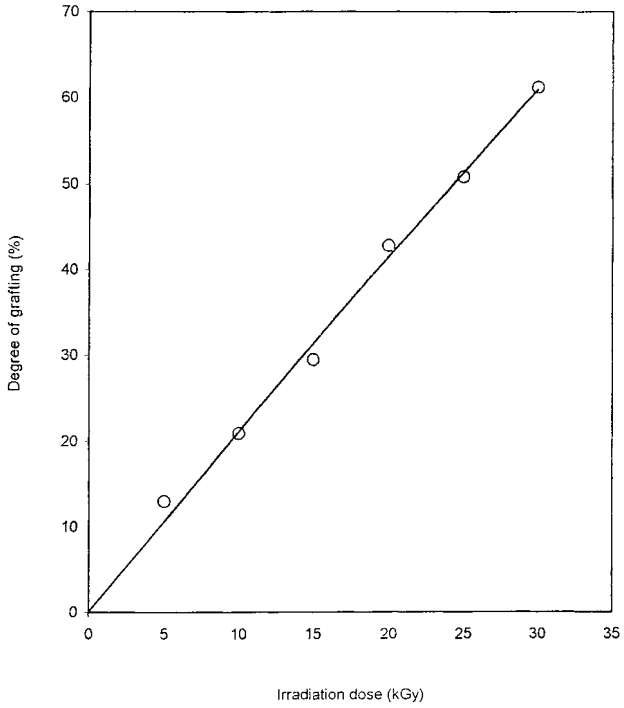


**Figure 1.** Variation of the degree of grafting with irradiation dose. Grafting conditions are: styrene concentration, 5.77 mol $l^{-1}$; solvent, dichloromethane; dose rate, 1.32 kGy $h^{-1}$; temperature, ambient; atmosphere, nitrogen; film thickness, 90 μm.

swelling of the grafted layers and monomer diffusion are enhanced and as a result longer polystyrene grafted chains are obtained. However, dilution of styrene with methanol, which has high chain transfer constant (0.296)[35] and is an electron donor, causes a rapid termination in growing chains which is enhanced by the reduction in monomer diffusion. Such reduction is due to the increase in the viscosity of the grafting mixture enhanced by the insolubility of polystyrene homopolymer formed in the grafting mixture. Thus, low levels of grafting are obtained and short grafts are formed. Moreover, in benzene, the resonance stabilization effect of the benzene ring, which acts as an energy-transfer agent, resulted in low degree of grafting due to the consumption of energy of irradiation. Similar behaviour was observed when the same three solvents were used to dilute styrene during its grafting onto PFA and FEP films.[33,34] Based on the results obtained from this study, dichloromethane was chosen as a diluent for styrene in the present grafting system.

*Irradiation dose*

Figure 1 shows the variation of the degree of grafting of styrene onto PTFE films with the irradiation dose and at an initial concentration in the starting solution of 5.77 mol $l^{-1}$ in dichloromethane. As can be seen, the degree of grafting increases gradually with increase in the irradiation dose within the limits of the studied values (5–30 kGy). This behaviour can be attributed to the increase in the number of radicals formed in the grafting system. Consequently, the rate and the degree of grafting increase with increase in the irradiation dose.

*Dose rate*

The variation of the degree of grafting with the dose rate at a total irradiation dose of 20 kGy is shown in Fig 2. The degree of grafting was found to decrease with the increase in the dose rate. It is well known that irradiation dose rate plays an important role in the grafting process because of its effect on the survival of the formed radicals and the extent of monomer diffusion through the polymer matrix. At low dose rates, monomer diffusion through the grafted layers is facilitated and the lifetime of the radicals formed is long enough to give long chain grafts. However, as the dose rate increases, the radicals formed tend to decay by recombination, leading to fast termination and/or degradation of the growing polystyrene chains. Subsequently, a decrease in styrene diffusion and its concentration in the internal grafting layers takes place, and thereafter short chain grafts are formed.

*Monomer concentration*

Figure 3 shows the variation of the final degree of grafting with monomer concentration, which represent the initial concentration in the starting solution. The degree of grafting is found to increase dramatically with the increase in styrene concentration in the starting solution until it reaches a maximum value at a concentration of 5.77 mol $l^{-1}$ and falls sharply as the concentration is further increased. Simultaneous grafting of styrene onto PTFE films was found to be

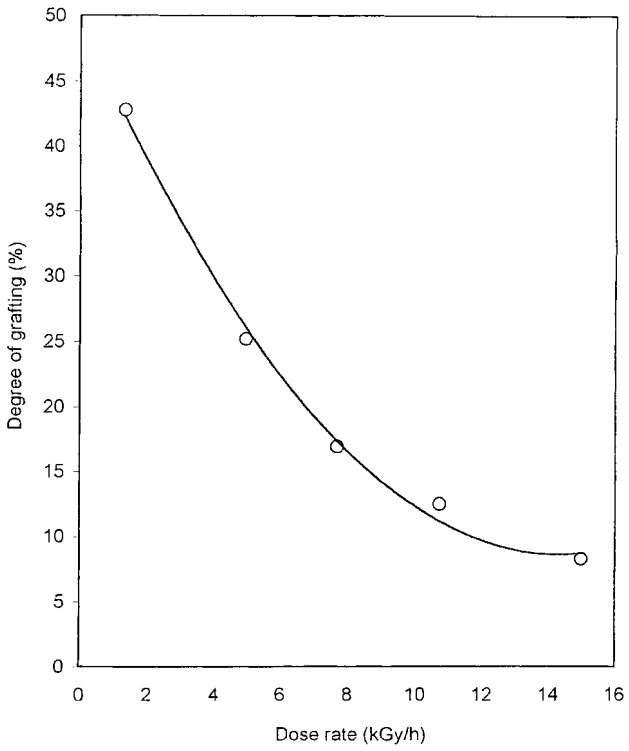


**Figure 2.** Variation of the degree of grafting with dose rate. Grafting conditions are as follows: styrene concentration, 5.77 mol $l^{-1}$, total irradiation dose, 20 kGy. The rest of grafting conditions is similar to Fig 1.

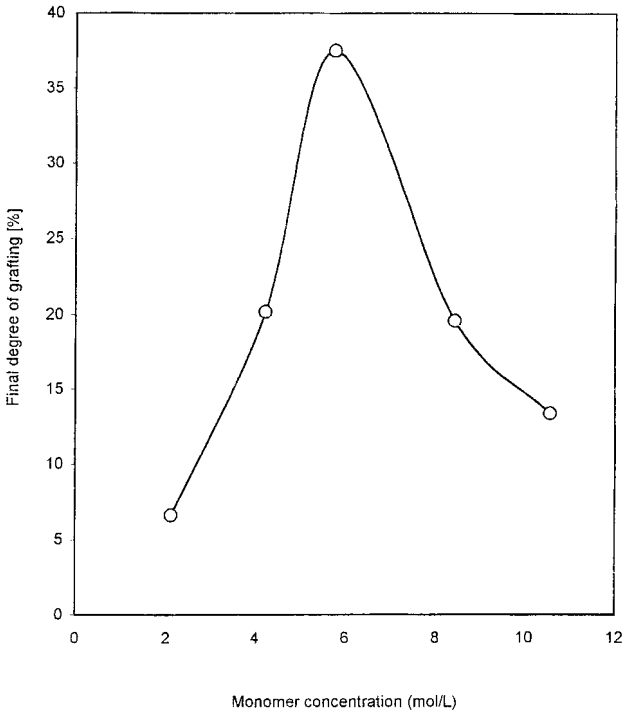


**Figure 3.** Variation of the final degree of grafting with monomer concentration. Grafting conditions are as follows: total irradiation dose, 20 kGy; solvent, dichloromethane. The rest of grafting conditions is similar to Fig 1.

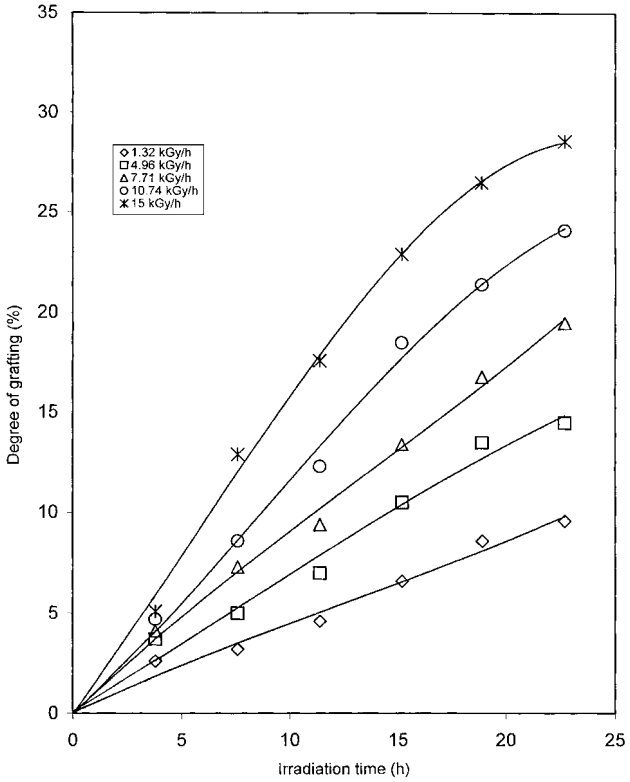


**Figure 4.** Degree of grafting versus irradiation-time curves at various dose rates: ◇, 1.32 kGy $h^{-1}$; □, 4.96 kGy $h^{-1}$; △, 7.71 kGy $h^{-1}$; ○, 10.74 kGy $h^{-1}$; *, 15 kGy $h^{-1}$. Grafting conditions are as follows: styrene concentration, 2.11 mol $l^{-1}$; solvent, dichloromethane. The rest of grafting conditions is similar to Fig 1.

a diffusion-controlled process.[36] Therefore, the increase in the degree of grafting in this system can be reasonably attributed to the increase in the styrene diffusion and its concentration in the grafting layers. When the styrene concentration in the styrene solution increases further, homopolymer formation is enhanced and the diffusion of styrene is hindered. As a result, the final degree of grafting falls sharply. However, the degree of grafting is found to be controlled by the number of radicals formed. Therefore, it can be concluded that the degree of grafting of styrene in the present system depends not only upon the number of radicals formed but also on the diffusion of styrene through the polymer matrix and its concentration in the grafting layers.

## Grafting kinetics

Figure 4 shows the degree of grafting and irradiation versus time curves at various dose rates, an initial monomer concentration in the starting solution of 2.11 mol $l^{-1}$ in dichloromethane and at ambient temperature. The degree of grafting increases for all dose rates with the increase in irradiation time. However, it tends to level off at higher irradiation times. Moreover, the higher the dose rate, the higher is the initial rate of grafting in the range of studied initial monomer concentration in the starting solution. The initial rate of grafting was determined graphically from Fig 4. The variation of the initial rate of grafting with the dose rate is presented in Table 2. As can be seen, the initial rate of grafting increases with the increase in the dose rate. The log–log relationship between the initial rate of grafting and the dose rate is shown in Fig 5 and a linear relationship is obtained. The dependence of initial rate of grafting ($dG_0/dt$) on the dose rate is found to be of the order of about 0.6 and this relation can be expressed as

$$\frac{dG_0}{dt} \alpha [D]^{0.6} \qquad (2)$$

where $dG_0/dt$ is the initial rate of grafting, $G_0$ is the degree of grafting at time $t$ and [D] is the dose rate. The exponent of the dose rate is found to be marginally higher than that of graft copolymerization of styrene onto polyethylene (0.5) in which polymerization was found to be terminated by usual bimolecular coupling.[37] This may be due to the use of styrene without further purification, which leads to termination of some of the growing chains by chain transfer to some impurities present in the grafting medium. It can be concluded that grafting in this system is strongly dependent upon the efficiency of free radical formation in PTFE film.

Figure 6 shows the degree of grafting versus irradiation-time curves at various initial styrene concentrations in the starting solution and at a constant dose rate of 1.32 kGy $h^{-1}$. The degree of grafting is found to increase with increase in the irradiation time. The variation of the initial rate of grafting, which is graphically calculated from Fig 6, versus the initial monomer concentration in the starting solution, is

**Table 2.** Initial rate of grafting of styrene[a] onto PTFE films at ambient temperature and various dose rates

| *Dose rate [D] (kGy h$^{-1}$)* | *Initial rate of grafting, $dG_0/dt = G$ (%/h)* |
|---|---|
| 1.32 | 0.69 ± 0.040 |
| 4.96 | 0.98 ± 0.058 |
| 7.71 | 1.08 ± 0.064 |
| 10.74 | 1.23 ± 0.074 |
| 15.00 | 1.35 ± 0.081 |

[a] Initial concentration in the starting solution 2.11 mol l$^{-1}$.

presented in Table 3. It is found that the initial rate of grafting increases with increase in the initial styrene concentration in the range 2.11–5.77 mol l$^{-1}$ and drops sharply at higher styrene concentrations. These results were confirmed from the log–log plot of the relationship between the initial rate of grafting and the styrene concentration (initial concentration in the starting solution) shown in Fig 7. The initial rate of grafting was found to increase linearly with the increase in the styrene concentration in the range 2.11–5.77 mol l$^{-1}$, but it drops sharply as the concentration increased further. Similar behaviour was also observed upon grafting of styrene in dichloromethane onto PFA and FEP films.[33,34] The dependence of the initial rate of grafting on the initial styrene concentration in the starting solution [M] was found to be of the order of 1.7 and can be expressed as

$$\frac{dG_0}{dt} \alpha [M]^{1.7} \qquad (3)$$

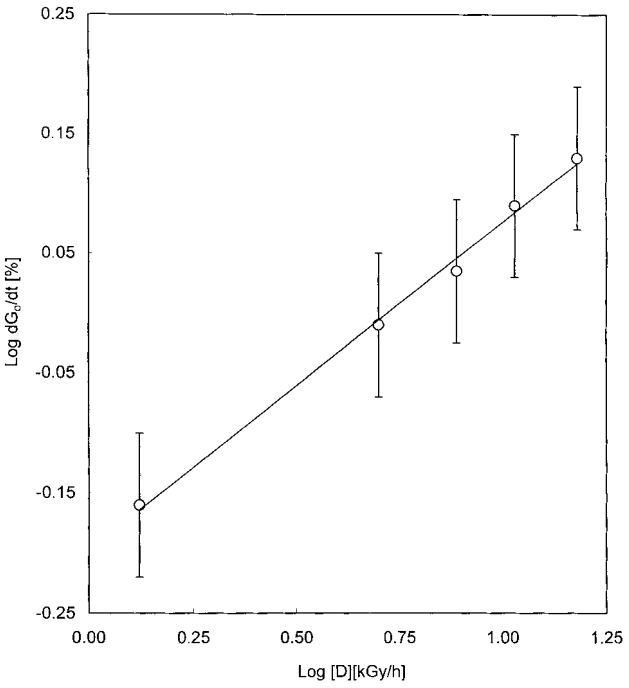


**Figure 5.** Log–log plots of the initial rate of grafting versus the dose rate. Grafting conditions are as follows: styrene concentration, 5.77 mol l$^{-1}$; solvent, dichloromethane. The rest of grafting conditions is similar to Fig 1.

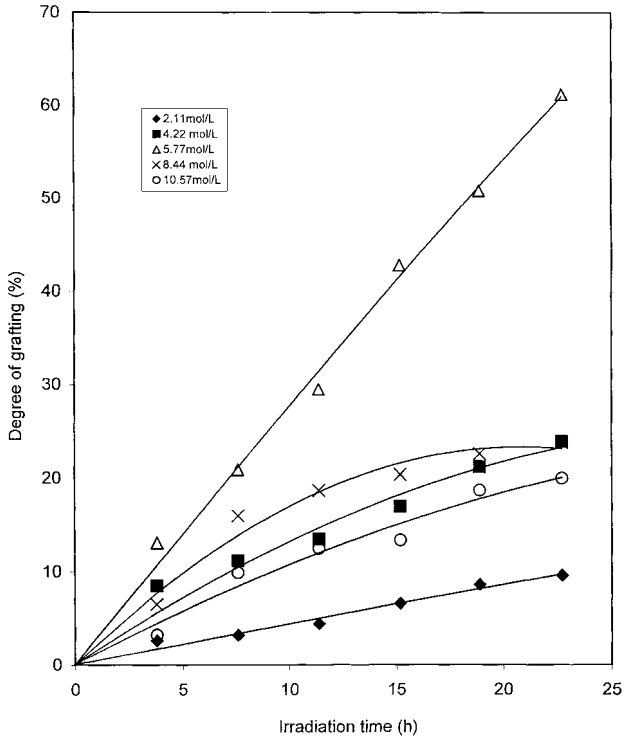


**Figure 6.** Degree of grafting versus irradiation-time curves at various styrene concentrations in dichloromethane. The rest of grafting conditions is similar to Fig 1.

Figure 8 shows the relationship between the degree of swelling of the original PTFE film and the monomer concentration. The degree of swelling was found to increase with increase in the monomer concentration from 2.11 to 5.77 mol l$^{-1}$ despite its low value, as PTFE film is well known to scarcely swell in monomers and solvents. Above 5.77 mol l$^{-1}$, the degree of swelling tends to drop. Because the initial rate and the final degree of grafting were found to have maximum values at an initial styrene concentration in the starting solution of 5.77 mol l$^{-1}$, it can be suggested that the kinetics are critically controlled by the rate of diffusion of the styrene into the PTFE film. Moreover, grafting starts at the surface of the film and proceeds internally towards the middle of the film by successive diffusion of the monomer through the swollen grafted layers until a swelling equilibrium is reached at a concentration of 5.77 mol l$^{-1}$. Based on the fact that a

**Table 3.** Initial rate of grafting of styrene onto PTFE films at various monomer concentrations, ambient temperature and a dose rate of 1.32 kGy h$^{-1}$

| *Monomer conc [M] (mol l$^{-1}$)* | *Initial rate of grafting, $dG_0/dt = G$ (%/h)* |
|---|---|
| 2.11 | 0.66 ± 0.04 |
| 4.22 | 2.24 ± 0.13 |
| 5.77 | 3.45 ± 0.21 |
| 8.44 | 1.70 ± 0.10 |
| 10.57 | 0.84 ± 0.05 |

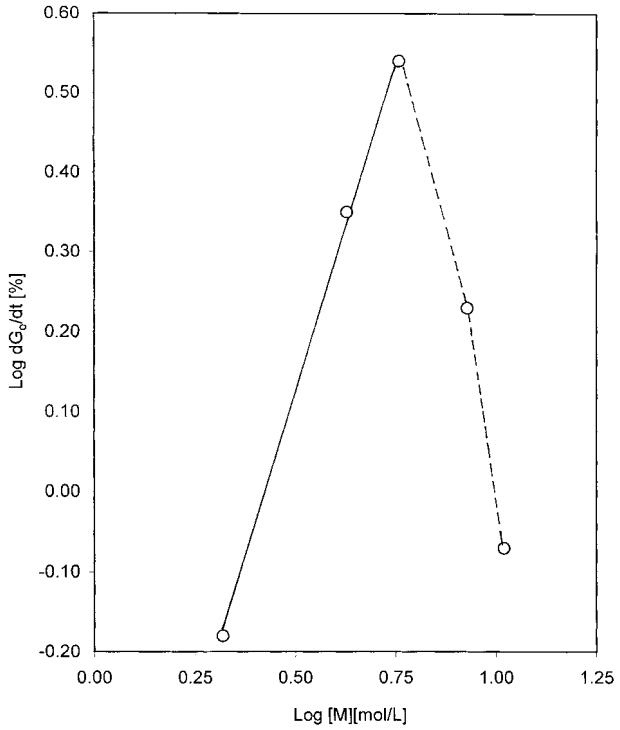


**Figure 7.** Log–log plots of the initial rate of grafting versus monomer concentration. Grafting conditions are as follows: dose, 20 kGy; solvent, dichloromethane. The rest of grafting conditions is similar to Fig 1.

polymer swollen in a solvent represents a medium of high viscosity, the high dependence of the initial rate of grafting on the initial monomer concentration in the starting solutions suggests that monomer diffusion is strongly dependent upon the viscosity of the grafting medium. Combining equations (1) and (2), allows the

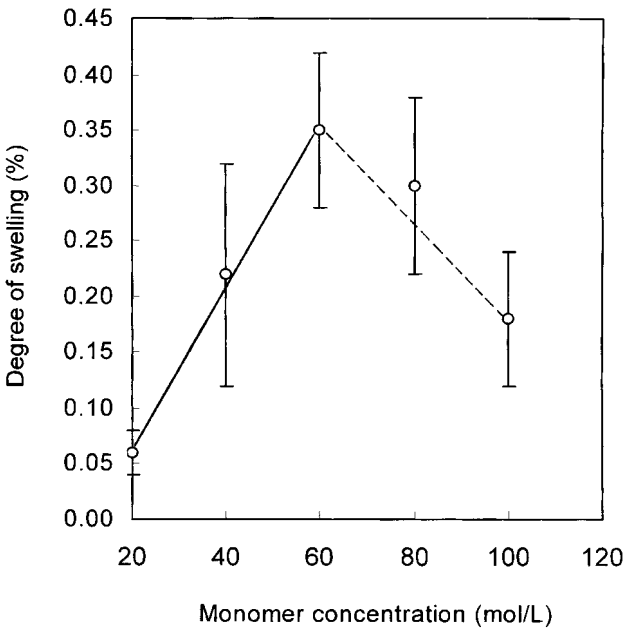


**Figure 8.** Relationship between the degree of swelling of PTFE film and monomer concentration. Swelling conditions are as follows: temperature, ambient; time, 4 days.

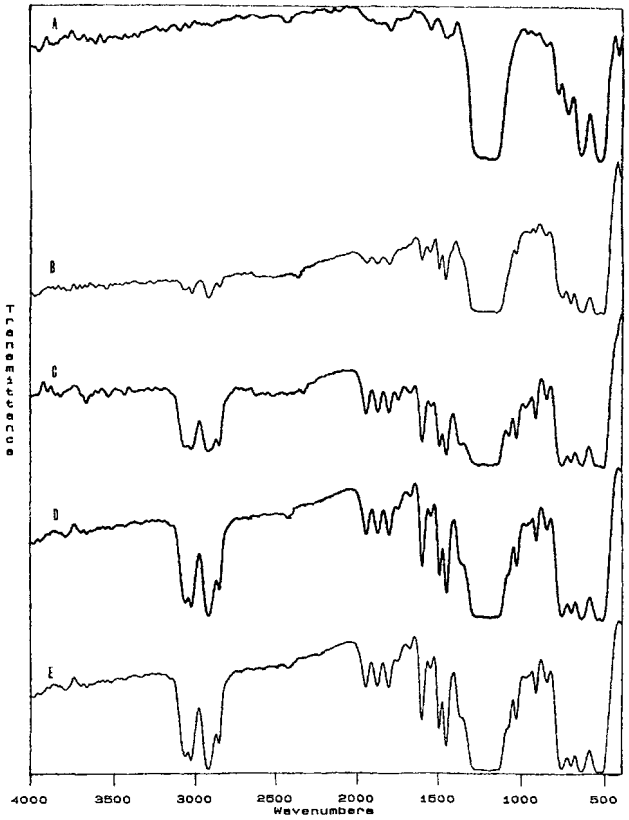


**Figure 9.** Typical FTIR-ATR spectra of original PTFE (A) and grafted PTFE films having various degrees of grafting: (B) 5%; (C) 18.5%; (D) 24% and (E) 36%.

grafting reaction in the present system to be represented by the correlation

$$\frac{dG_0}{dt} \propto [D]^{0.6}[M]^{1.7} \quad (4)$$

It can be concluded that the kinetics of graft copolymerization in the present system depend not only upon the efficiency of the radicals initiating the grafting but also upon the availability of the monomer molecules in the grafting layers.

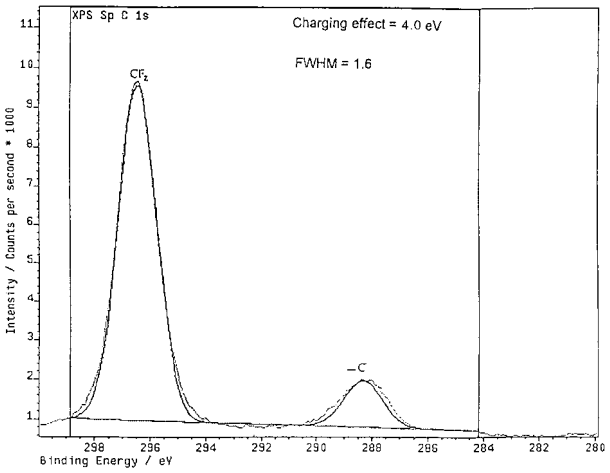


**Figure 10.** ESCA narrow scan of C1s of the original PTFE film.

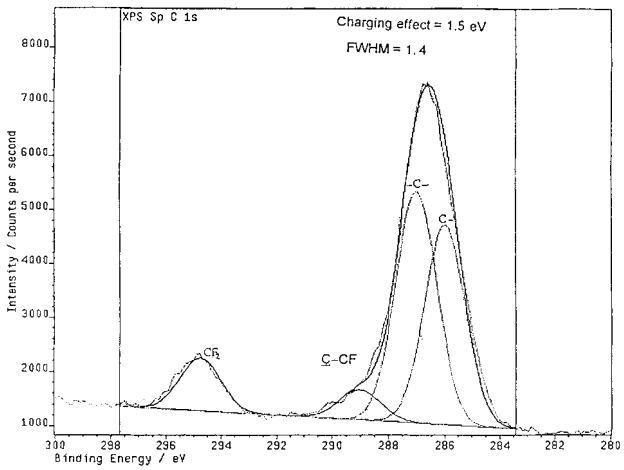


**Figure 11.** ESCA narrow scan of C1s of 36% grafted PTFE film.

## Characteristics of the grafted films

Typical FTIR-ATR spectra of original and grafted PTFE films having various degrees of grafting are shown in Fig 9. The characteristics bands at 1150–1250 $cm^{-1}$ are assigned for stretching vibration of the $CF_2$ groups present in the original PTFE film. The presence of the benzene rings of polystyrene grafts is established by the =C—H stretching vibration at 3050 $cm^{-1}$ and the skeletal C=C in-plane and stretching vibrations at 1500 $cm^{-1}$ and 1600 $cm^{-1}$, respectively. The mono-substitution of the benzene ring is confirmed by the aromatic out-of-plane C—H deformation band at 860 $cm^{-1}$, C—H out-of-plane bending overtone and the combination band patterns in the 1660–2000 $cm^{-1}$ region. The absorption bands at 2800–2900 $cm^{-1}$ and 2900–3000 $cm^{-1}$ are assigned to symmetric and asymmetric stretching of aliphatic $CH_2$ groups, respectively. It is clear that the features of the spectra of the grafted films confirm the successful grafting of styrene onto the PTFE backbone. The variation in the intensity of polystyrene characteristic bands reflects the difference in the degrees of grafting.

The chemical structures of the original and 36% grafted PTFE films were investigated by electron spectroscopy for chemical analysis (ESCA). The ESCA narrow scan of C1s of the original PTFE film is presented in Fig 10. A major peak at 291.5 eV represents F—C—F which is the basic unit in the structure of PTFE film, and a minor peak at 284.5 eV from the terminal carbon (C—) can be seen. The shift in the binding energy of $CF_2$ from that of $CH_2$ reported in the literature is due to the chemical shift arising from the electron attraction towards the fluorine atoms, which equals 8 eV. Such results are in good agreement with those obtained by Scherer *et al*[38] upon investigation of some radiation-grafted commercial membranes such as Permion 4010 and 5010 (RAI Inc, Hauppauge, NY, USA). The F/C ratio is found to be 2.09, which is in a good agreement with the theoretical value of 2.

Figure 11 depicts the ESCA narrow scan of C1s of the 36% grafted PTFE film. When compared with Fig 10, it can be seen that the intensity of the C1s peak increased and that for C1F decreased, and as a result the F/C ratio fell to 0.26. The deconvolution of the spectrum shows four component peaks having corrected binding energies of 293.3, 287.5, 285.5 and 284.5 eV representing $CF_2$, C—CF, C— and C—, respectively. The emergence of the C—CF peak confirms the grafting of the styrene onto the main chains of the PTFE film. The incorporation of polystyrene side chain grafts enhances the rupture of —CF— bonds near the surface and introduces hydrocarbon components in the form of aliphatic (—$CH_2$—CH=) and aromatic (—$C_6H_5$) groups into the fluorinated structure of the PTFE film. Consequently, a considerable increase in the intensity of C1s followed by a decrease in the intensity of the F1s peak takes place. It is important to mention that the difficulty in the specific determination of —C— and C— of aliphatic (—$CH_2$—CH=) and aromatic —($C_6H_5$) groups in the polystyrene incorporated in the grafted film is due to the minor chemical shift differences in these carbon atoms.[39] Details of chemical structure investigations of the grafted PTFE films having various degrees of grafting by ESCA have been reported elsewhere.[40]

Diffractograms of the original and grafted PTFE films having various degrees of grafting are shown in Fig 12. It can be seen that a remarkable decrease in the degree of crystallinity of the grafted films takes place as

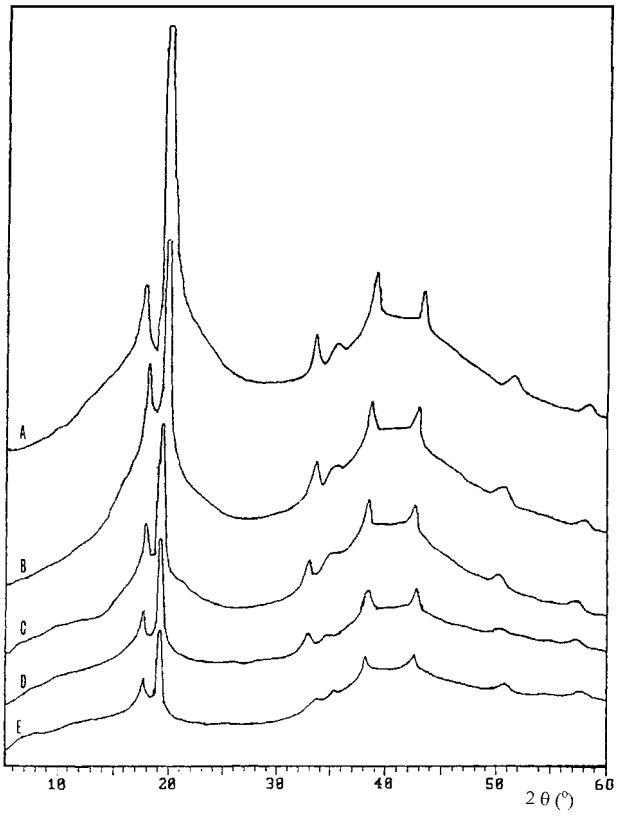


**Figure 12.** Diffractograms of original PTFE (A) and grafted PTFE films having various degrees of grafting: (B) 5%; (C) 18.5%; (D) 24%; and (E) 36%.

a result of grafting, and that the extent of such a decrease depends mainly on the degree of grafting. It is obvious that higher degrees of grafting are accompanied by lower degrees of crytallinity and vice versa, as illustrated from the inverse proportional relationship between the peak intensity and the degree of grafting. Moreover, the effect of grafting on the crystallinity for all grafted films shows no shift in the angle ($2\theta$) compared to the original (non-grafted) film, which may reflect that no changes in the chemical structure of the bulk of PTFE are induced by radiation and that no new phase is formed upon grafting. The reduction in the degree of crystallinity is mostly due to the increase in the intermolecular distance between PTFE polymer chains with increase of the polystyrene content. These results suggest that the reduction in the crystallinity of the grafted films can be attributed to the dilution of the cystalline structure with the amorphous polystyrene grafts, which increase gradually with the degree of grafting.

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